Electrocatalytic Hydrogen Evolution in Acidic Water with Molecular Cobalt Tetraazamacrocycles.

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Supporting Figures

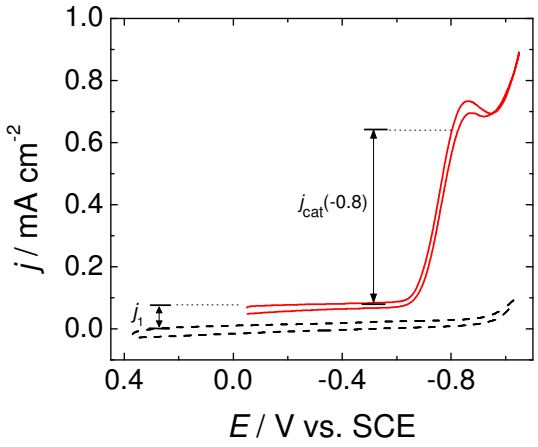

Figure S1. Rotating disk electrode voltammogram at 400 rpm in 0.1 M phosphate buffer at pH 2.2 in the absence (—) and presence (—) of 0.3 mM **2**. j_1 is the plateau current density for the $Co^{III/II}$ reduction. j_{cat}(E) is the catalytic current density and is measured from j_1. j_{cat}(–0.8) = 0.54 mA cm^{-2} as shown in the figure. (0.1 M $NaClO_4$ supporting electrolyte, scan rate = 0.025 V/s, Ar atmosphere).

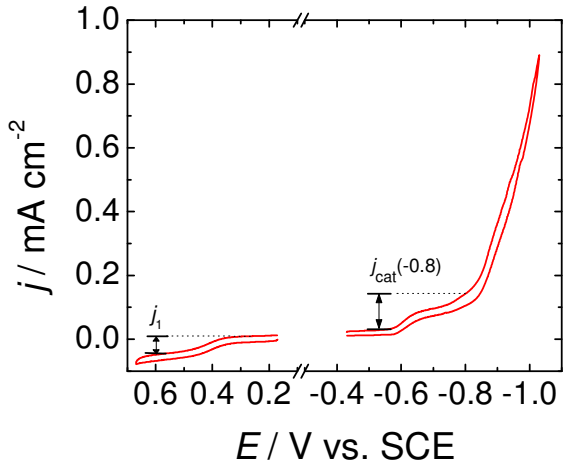

Figure S2. Rotating disk electrode voltammogram at 400 rpm in 0.1 M phosphate buffer at pH 2.2 with 0.3 mM **3**. j_1 is the plateau current density for the $Co^{III/II}$ reduction. j_{cat}(E) is the catalytic current density and is measured from j_1 as shown. j_{cat}(–0.8) = 0.14 mA cm^{-2} as shown in the figure. (0.1 M $NaClO_4$ supporting electrolyte, scan rate = 0.025 V/s, Ar atmosphere).

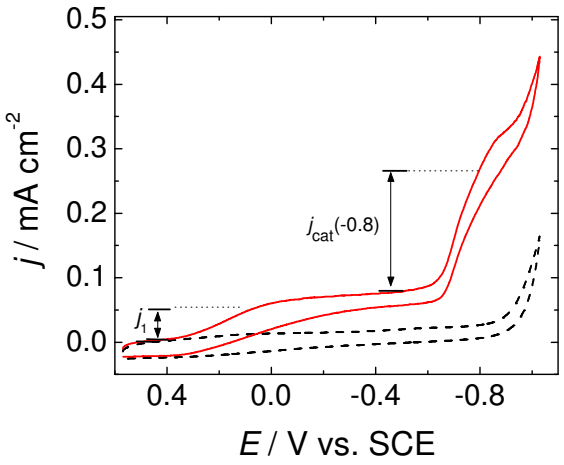

Figure S3. Rotating disk electrode voltammogram at 400 rpm in 0.1 M phosphate buffer at pH 2.2 in the absence (—) and presence (—) of 0.3 mM **4**. j_1 is the plateau current density for the $Co^{III/II}$ reduction. $j_{cat}(E)$ is the catalytic current density and is measured from j_1. $j_{cat}(-0.8)$ = 0.19 mA cm^{-2} as shown in the figure. (0.1 M $NaClO_4$ supporting electrolyte, scan rate = 0.025 V/s, Ar atmosphere).

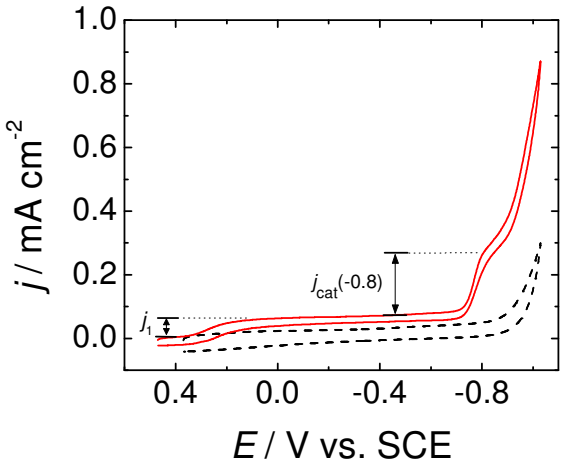

Figure S4. Rotating disk electrode voltammogram at 400 rpm in 0.1 M phosphate buffer at pH 2.2 in the absence (—) and presence (—) of 0.3 mM **5**. j_1 is the plateau current density for the $Co^{III/II}$ reduction. $j_{cat}(E)$ is the catalytic current density and is measured from j_1. $j_{cat}(-0.8)$ = 0.19 mA cm^{-2} as shown in the figure. (0.1 M $NaClO_4$ supporting electrolyte, scan rate = 0.025 V/s, Ar atmosphere).

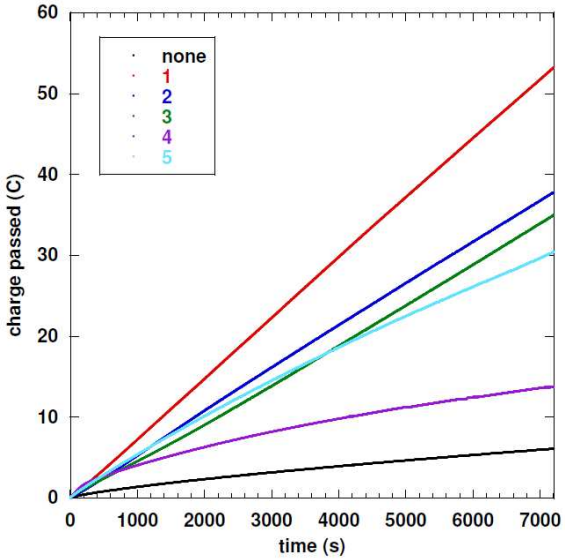

Figure S5. Sample graphs of charge passed as a function of time over 2-h controlled-potential electrolysis experiments in the absence or presence of catalysts **1–5** at a 0.3 mM concentration. (0.1 M $NaClO_4$, 0.1 M pH 2.2 phosphate buffer, –0.93 V).

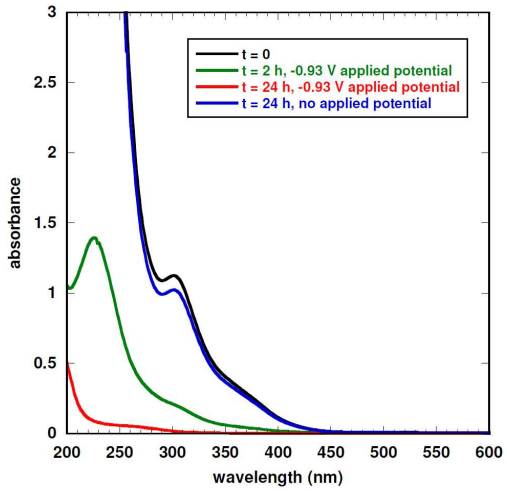

Figure S6. UV-vis spectrum of the solution in the half-cell containing the working electrode and 0.3 mM **1** before (black) and after a 2-h (green) and 24-h bulk electrolysis period (red). For comparison a solution of 0.3 mM **1** allowed to stand for 24-h in the same buffer solution in the absence of an applied potential is shown (blue).

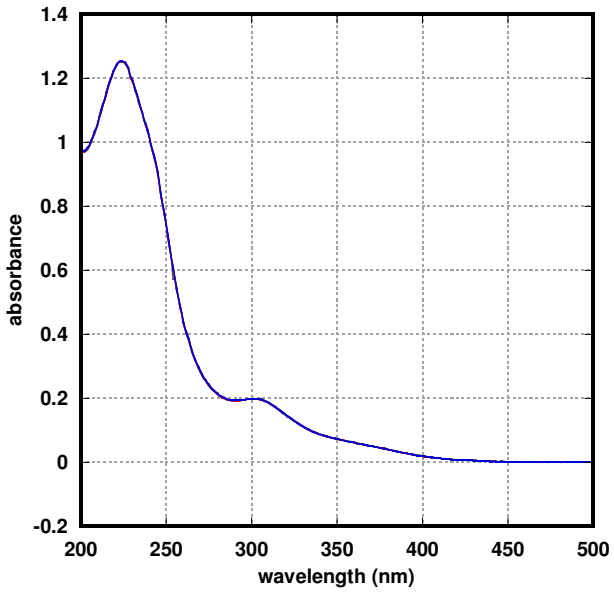

Figure S7. Complex **1** was dissolved in pH 2.2 phosphate buffer solution containing 0.1 M [*n*-Bu_4N][ClO_4] at a concentration of 0.05 mM. UV-vis spectra were collected over a 2-h period. Spectra were observed to overlay, and no detectable decomposition or loss of absorbance was observed over this period.

Table S1. Charge passed, Volume H_2 measured, and corresponding Faradaic Efficiencies measured at different times during 24 controlled-potential electrolysis measurements.

Experiment	time	q^a / C	$V_{H2}{}^b$ / mL	f^c / %
1	24 h	295	30.2	80
2	6.3 h	93	10.5	89
	17.6 h	200	26.4	103
	24 h	295	32.0	86

[a]Cumulative charge passed during controlled-potential electrolysis. [b]Volume of H_2 measured. [c]Faradaic efficiency determined from dividing the measured volume of H_2 by the predicted volume from the cumulative charge passed.

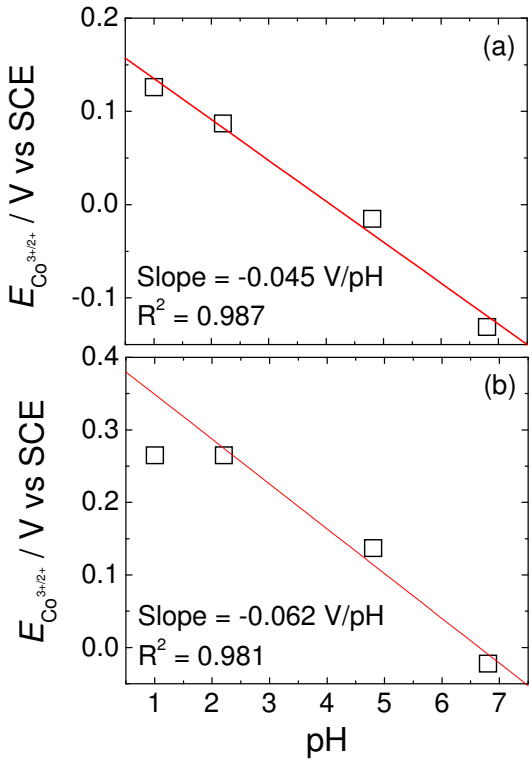

Figure S8. pH dependence of the $Co^{III/II}$ couple for complexes **2** (a) and **5** (b). The lines are linear fits to the data. For (b), the linear fit is only through the last three points – there is no pH dependence between pH 1 and pH 2.2.

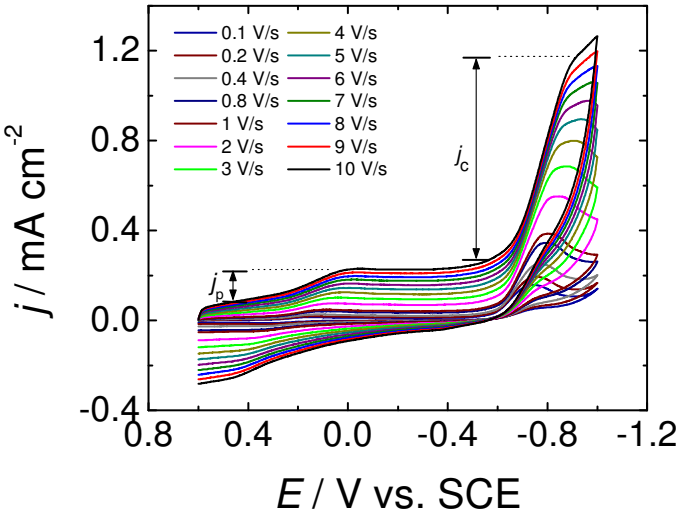

Figure S9. Cyclic voltammograms of 0.3 mM **1** in aqueous solutions at pH = 2.2 at multiple scan rates. j_p is the plateau current density for the $Co^{III/II}$ reduction at high scan rates. j_c is the catalytic current density measured from j_1, as shown. (0.1 M $NaClO_4$ supporting electrolyte, H_2 atmosphere).

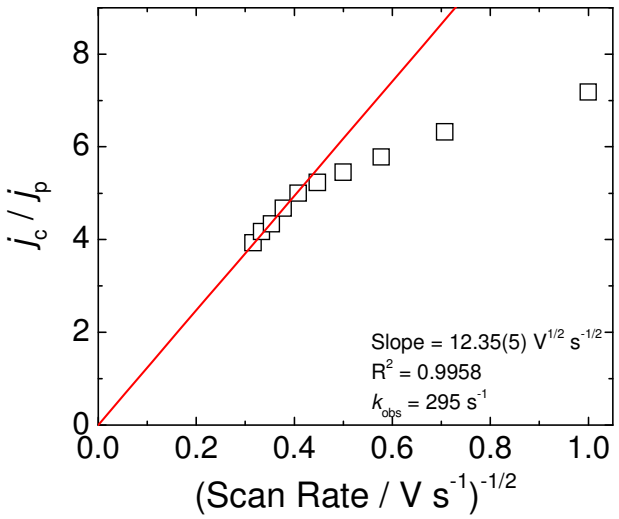

Figure S10. Scan-rate dependence of j_c/j_p for catalyst **1** in pH 2.2 aqueous solution. The data is linear in $\upsilon^{-1/2}$ for scan rates υ > 5 V/s. In this linear region, j_c is approximately constant and the k_{obs} is determined from the slope of a fit line according to Equation 2.